Supporting Information for

Ion irradiation enhanced Raman scattering on nanoporous copper

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SRIM simulation

Fig. S1. shows the SRIM simulation results of the damage distribution and ion concentration distribution in the 3 MeV Cu^+ ion-irradiated NPC ribbons at the dose of 3.36×10^{14} ions/cm^2. The parameter of the target density of the NPC ribbons was set as 30 percent of copper because the atom proportion of copper in the $Cu_{30}Zr_{65}Al_5$ precursor glassy ribbons was 30% (ignoring the slight change in volume after dealloying). The peak damage was approximately 1.5 dpa at the depth of 1300 nm and the average damage distribution during the Cu^+ ion implanting range (0-2500 nm) was 1dpa so as to avoid destroying the integral structure of NPC ribbons.

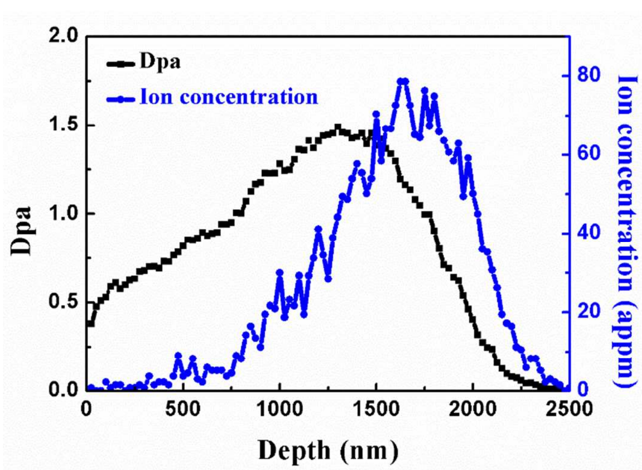

Fig. S1. SRIM simulation results of the damage distribution and ion concentration distribution in the 3 MeV Cu^+ ion-irradiated NPC ribbons at the dose of $3.36 \times 10^{14}\ ions/cm^2$.

Irradiation experiment

As Fig. S2. illustrates, the Cu+ ions are ionized through ion source by sputtering, and then accelerated after high-voltage electric field in accelerating cavity, and ultimately irradiate the surface of the target materials vertically. The NPC ribbons were bombarded with a 3 MeV Cu+ ion beam to fluence at 3.36×10^{14} ions/cm^2 under room temperature with a flux of ~10^{11} ions/cm^2/s. The chamber was evacuated to a base pressure of 2×10^{-4} Pa prior to ion irradiation and the molecular pump is constantly vacuuming during the whole irradiation experiment. The target material used in current study is the as-dealloyed NPC ribbons, which consists of pure copper only. As for the irradiation ions, only the Cu+ ions can finally bombard the surface of NPC ribbons and other kinds of ions with different charge-to-mass ratio will not reach the target after passing the bending magnet. Therefore, no other foreign ions and contaminants are introduced into the NPC ribbons.

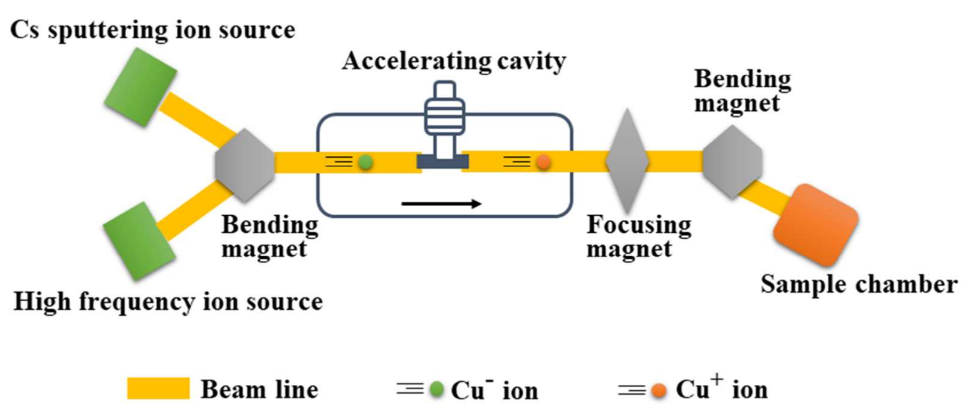

Fig. S2. The schematic diagram of the 1.7 MV tandem accelerator.

Characterization

Phases present in the as-spun $Cu_{30}Zr_{65}Al_5$ ribbons and the as-dealloyed nanoporous copper (NPC) ribbons were characterized by X-ray diffraction (XRD, Rigaku DMAX-RB-12KW, Cu-Kα radiation). The XRD results as shown in Fig. S3. confirm the successful fabrication of NPC from the metallic glass precursor. The characteristic amorphous halo completely disappears and sharp crystalline peaks representative of the face centered cubic (fcc) Cu arise.

Microstructures and compositions of the as-dealloyed NPC ribbons and Cu^{+} ion-irradiated NPC ribbons were characterized by scanning electron microscopy (SEM, FEI NanoSEM 430) equipped with an energy dispersive X-ray spectrometer (EDX) and transmission electron microscope (TEM, Hitachi H9000). EDX analysis on the as-dealloyed and ion-irradiated NPC ribbons (as shown in Fig. S4.) was conducted to guarantee that the chemical composition stayed unchanged after irradiation and no other extra impurity was introduced. For TEM research, the NPC ribbons were first dispersed by sonication in ethanol for a few seconds. Then a few drops of resultant suspension were put onto holey carbon TEM grids using the pipette and allow it to dry at room temperature. TEM observations were performed at an accelerating voltage of 300 kV.

Before Raman experiments, 2 μL R6G aqueous solution with the concentration of 10^{-4} M and 10^{-2} M was dropped on the as-dealloyed and ion-irradiated NPC substrates and the glass slide substrate, respectively. After the droplet dried, it formed a stain with the area of about 5 mm^2. The as-prepared samples were then subjected to the Raman tests. Both the normal Raman scattering (NRS) spectra of 10^{-2} M R6G on glass slides and surface enhanced Raman scattering (SERS) spectra of 10^{-4} M R6G on NPC substrates were acquired on the LabRAM ARAMIS confocal Raman microscope with the laser wavelength of 532 nm at a spectral resolution of 1.8 cm^{-1}. The laser beam size for the Raman measurements was set as 1 μm in diameter. More than 10 measurements were conducted from different regions for each sample. And during each measurement, the acquisition time of the spectrum was set to 6 seconds.

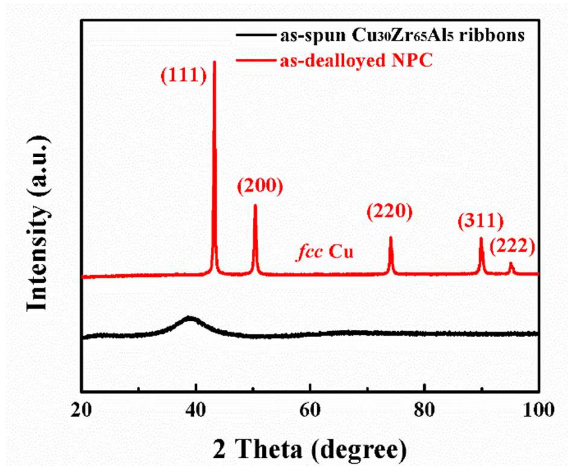

Fig. S3. XRD patterns of the as-spun $Cu_{30}Zr_{65}Al_5$ glassy ribbons and as-dealloyed NPC samples.

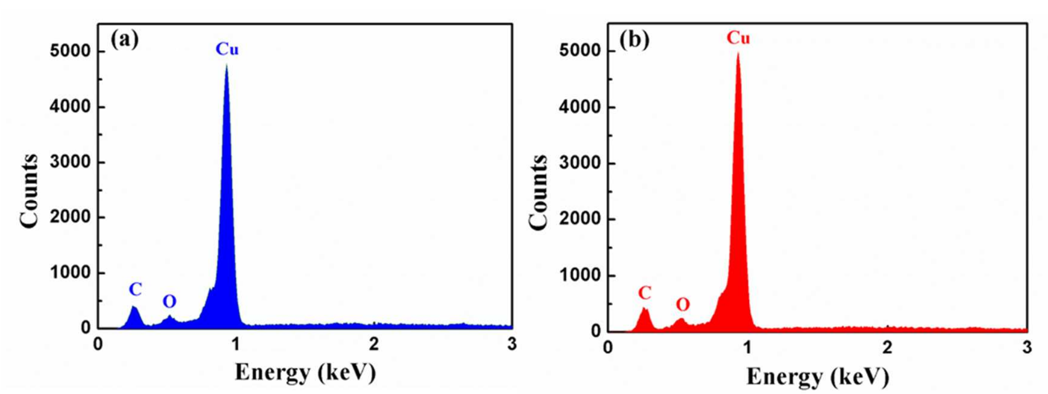

Fig. S4. EDX analysis of the (a) as-dealloyed NPC ribbons and (b) Cu^+ ion-irradiated NPC ribbons at the dose of $3.36 \times 10^{14}\ \mathrm{ions/cm^2}$.

Calculation for EF of NPC substrates

In order to calculate the EF of the as-dealloyed and ion-irradiated NPC substrates, we also measure the normal Raman scattering (NRS) spectra of 10^{-2} M R6G solution on glass slide substrates. The EF of NPC substrates is thus calculated by compared with the NRS spectra. The size of the laser beam spot is ~ 1 μm in diameter in all Raman tests. The effective number of R6G molecules can be estimated by the following formula

$$N = \frac{N_A M V_{solu} S_{sub}}{S_{laser}} \quad (1)$$

where N is the average number of corresponding R6G molecules excited by the laser beam in Raman test, N_A is the Avogadro constant, M is the molar concentration of the R6G solution, V_{solu} (2 μL in all tests) is the volume of R6G solution dropped on substrates, S_{sub} (~5 mm^2 in all tests) is the effective area of the substrates and S_{laser} (~1 μm in diameter in all tests) is the size of laser spot. Combined with the formula (1) in the manuscript, the EF can thus be calculated.

TEM Observation of SFTs

We do observe some stacking fault tetrahedrons (SFTs) in the NPC ligaments as shown in Fig. S5. However, the density of SFTs is relatively low and only affects the electronic structure of NPC substrates to some extent. The reason of the improved SERS performance of NPC substrates after ion irradiation is believed to be the surface roughening effect.

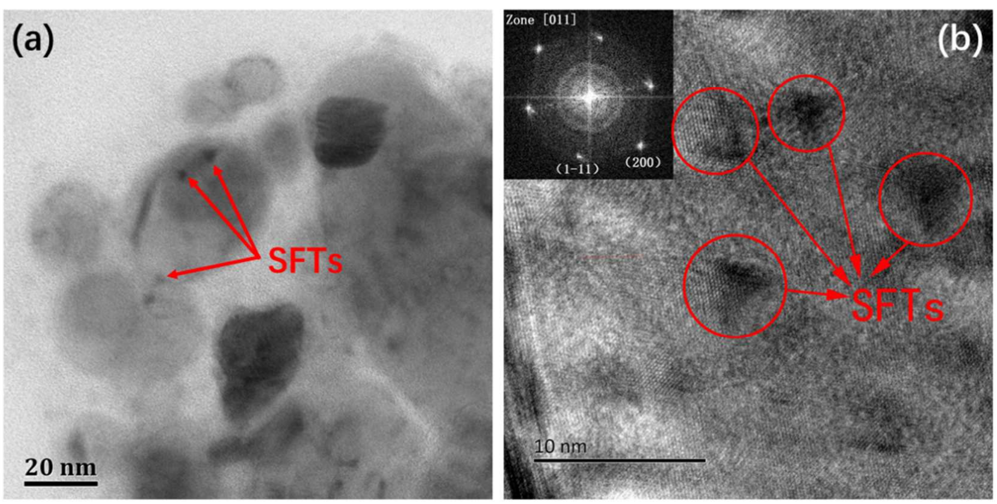

Fig. S5. (a) bright-field and (b) High-resolution TEM images showing the SFTs in the ligaments of ion-irradiated NPC samples.